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Metallic nanocluster materials: Separation, crystallization, pressure and magnetism .

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Abstract

One of the most interesting aspects of metallic nanoclusters is the electronic shell structure known to be present [1], resulting in discrete and molecular like energy levels, where the valence electrons of the core can occupy a new set of "superatomic" orbitals, analogous to atomic orbitals where a closed shell confers stability and the same spherical harmonics are exhibited [2]. The molecular like state of these clusters opens up the possibility to form new types of materials based on cluster building blocks. Various organically passivated metallic clusters are known to exhibit this electronic shell structure and crystallize into superstructures.

How the superatomic orbitals interact with one another under close proximity or how they are effected by external stimuli is of great interest for the development of these materials for advanced applications. Furthermore, improving the purity and separation of said building blocks is thus important for manufacture of high quality crystals for examination. Our work looks into these subjects for the advancement and development of cluster materials.

Separation

Synthesis of metallic nanoclusters often results in multiple size clusters requiring efficient and simple separation to obtain size pure samples for crystallization and analysis.

Here we show with the *Qian & Jin* [3] synthesis of Au_{25}^- & Au_{144} clusters can be simply and efficiently separated using a DCM:Hex:MeOH solvent liquor (Fig 1). This solvent mixture can be seen to be more effective than the original solvent separation method (Fig 2).

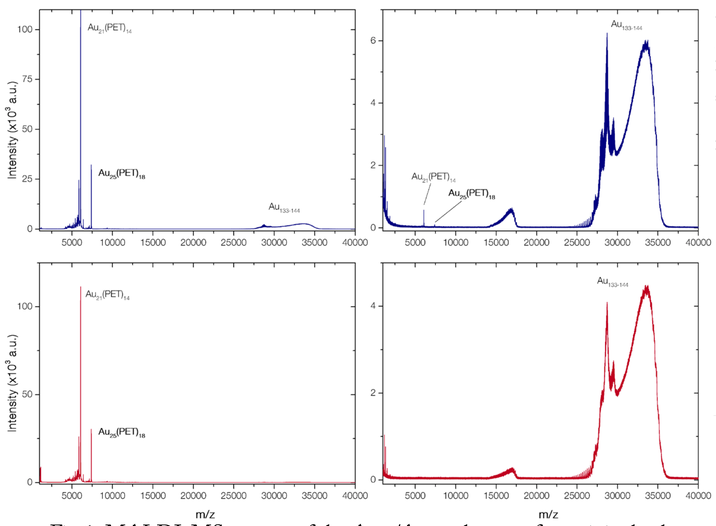

Fig 1: MALDI-MS spectra of the Au_{25}/Au_{144} clusters after original solvent separation method (blue), and after the DCM:Hex:MeOH method (Red).

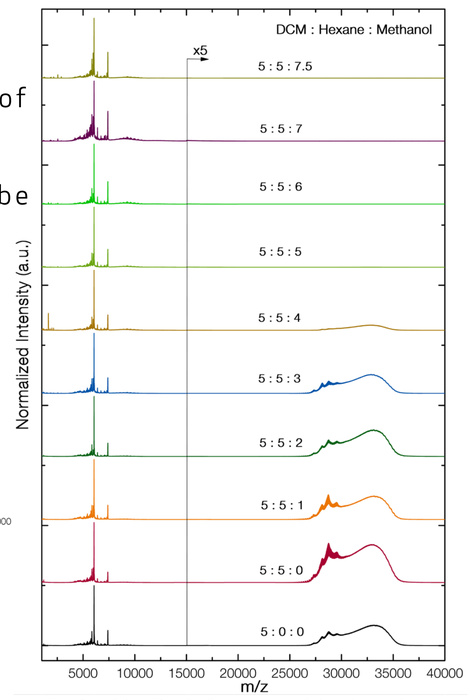

Fig 2: MALDI-MS spectra of the Au_{25}/Au_{144} cluster mixture in varying DCM:Hex:MeOH mixtures.

Pressure

The first experimental investigation on the effect of (isotropic) high pressure on the superatomic electronic structure of metallic clusters in the molecular state was conducted.

The experiment revealed both red and blue shifts at relatively low pressures (Fig 4) in the unique electronic spectra for the clusters studied. Cross-examining the shifts with the calculated transitions from previous TDTDFT calculations [2,4-7] it is suggested that the increased pressure upon the core affects the splitting of the super atomic orbitals and destabilizing the ligand states causing the observed shifts in the molecular absorbance spectra (Fig 3).

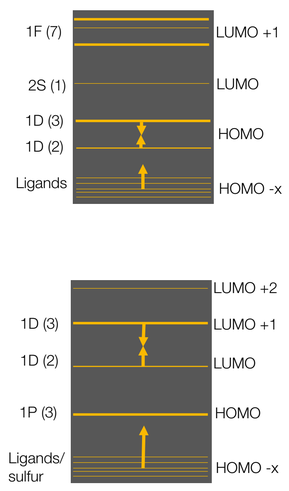

Fig 3: Diagram of suggested change to theoretical orbital energy levels

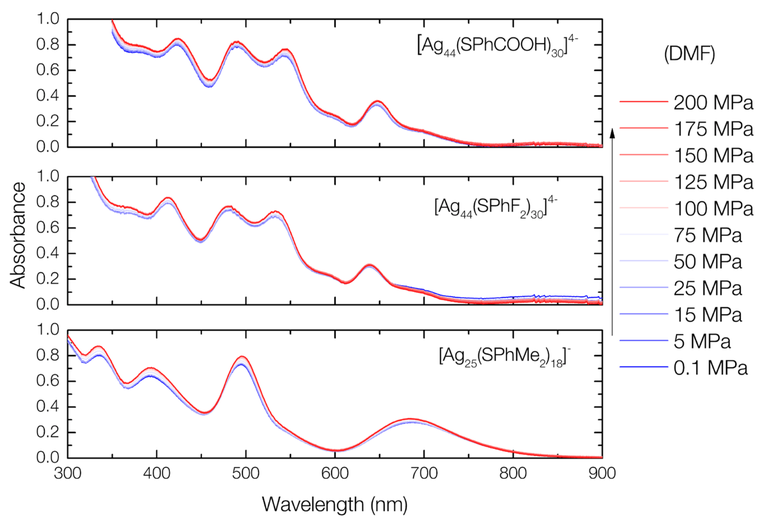

Fig4: UV-vis molecular absorbance spectra of metallic nanoclusters under increasing isotropic pressure.

Novel Crystal

Using efficiently separated Au_{25}^- clusters and a specific solvent liquor, clusters were oxidised to the charge neutral state and crystallized into a new Triclinic unit cell containing the co-solvent toluene (Fig 5) differing from the reported Au_{25}^0 orthorhombic unit cell [8].

The new crystal unit cell gives shows that the cause of deformation of the six octahedral $Au_2(SCH_2CH_2Ph)_3$ capping units of the cluster seen in both this cluster & the analogous anionic cluster crystal system is sterically related to the co-crystallization molecules and not formal charge of cluster.

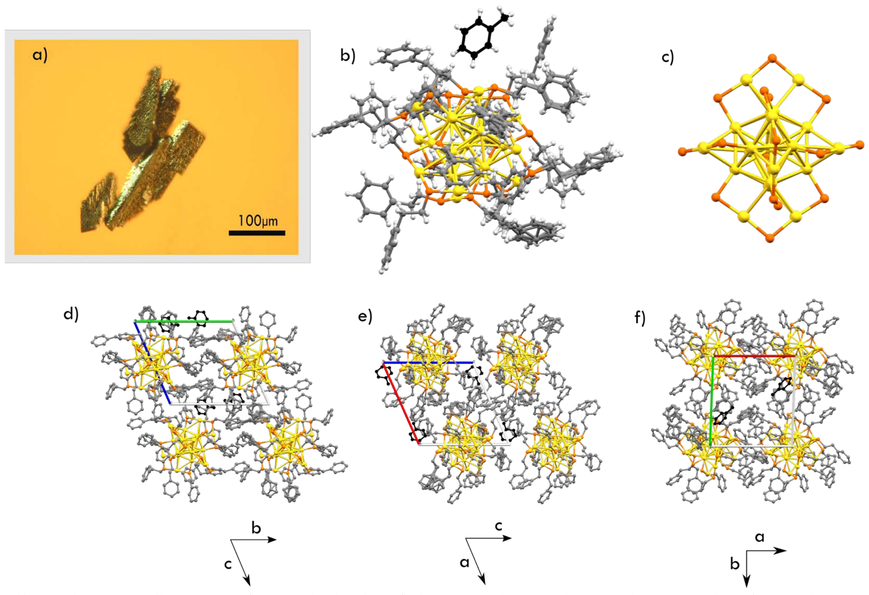

Fig 5: a) Optical image of new Au_{25}^0 crystals. b) Au_{25}^0 cluster with co-solvent toluene. c) Au_{25}^0 core showing the distorted $Au_2(SCH_2CH_2Ph)_3$ capping units (carbons removed for clarity). d-f) the unit cell viewed down the a,b & c-axis respectively.

Magnetism

It was postulated by *Knight* [9] and later by *Kresin & Ovchinnikov* [10] that the increased density of states generated by the superatomic orbitals in clusters could enhance superconductive (SC) condensate and that even a macroscopic SC current could be generated in an array of closely placed clusters.

SQUID magnetometry revealed no SC in any of the clusters observed however interesting phenomenon occurred with increasing cluster size (Fig 6).

$[Au_{25}(SCH_2CH_2Ph)_{18}]^0$ crystals gave a paramagnetic signal due to the oxidation of the cluster.

$[Ag_{44}(SPHCOOH)_{30}]^{4-}$ crystals exhibit diamagnetism due to the closed electronic shell. An interesting increase in diamagnetism can be observed at low temperatures (20 K).

$[Au_{144}(SCH_2CH_2Ph)_{60}]^0$ crystals exhibit an antiferromagnetic exchange interactions, C= 301.11 emu K / mol, Θ = -721.5 K.

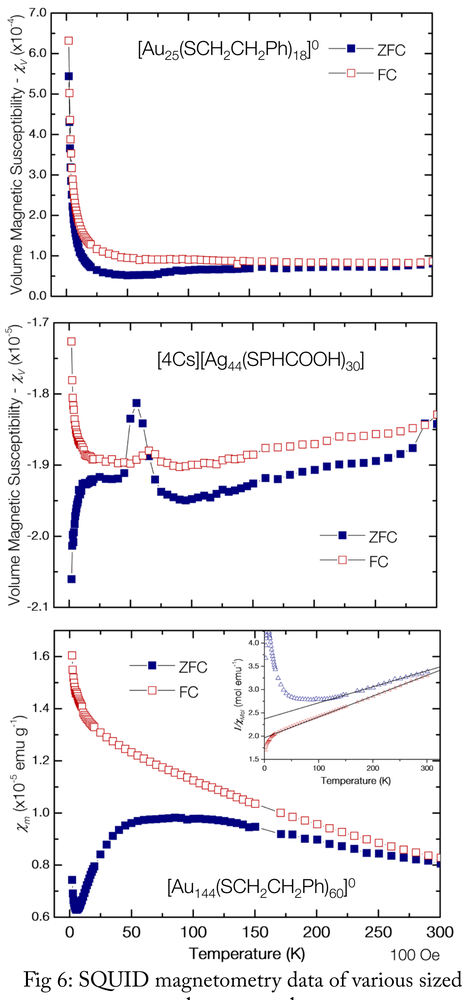

Fig 6: SQUID magnetometry data of various sized cluster crystals.

References

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